

PATENT SPECIFICATION

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Inventor: JOHN CLIFFORD WILSON

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COMPETE SPECIFICATION

Improvements in or relating to Coated Films

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to coated films, and more particularly to synthetic organic thermoplastic films having a heat-sealable coating and a process for the production of heat-sealable coated films.

It is known that when such films are coated with layers of suitably chosen material in order to render them heat sealable, such as layers of vinylidene chloride copolymers, they have such a high tendency to pick up electrostatic charges that they are unsuitable for use of many types of automatic packaging machinery. It is therefore desirable to include in the heat-sealable layer a substance imparting anti-static properties to the coated film.

Unfortunately, when the substances which are normally used to impart anti-static properties to films are applied in the form of a surface coating to films of polyolefines, particularly polypropylene films, in amounts sufficient to impart worthwhile improvements in anti-static properties, only very poor adhesion to the base film is obtained unless the film is first coated with an anchor coat of, for instance, a substantially water-insoluble thermosetting resin. It is both costly and inconvenient to have to use such an anchor coat.

It is an object of the present invention to provide a process for coating thermoplastic films with heat-sealable layers having good anti-static properties without the necessity of employing an anchor coat. It is another object of this invention to provide improved coated films.

Accordingly, we provide a process which comprises coating the surface of a synthetic

organic thermoplastic film with an aqueous dispersion of a heat-sealable polymer, said dispersion containing from 0.5% to 5.0% by weight of its polymer solids content of an ionic anti-static agent comprising the metal, ammonium or amine salt of the sulphonated condensation product of formaldehyde and an aromatic hydrocarbon, and thereafter drying the coated film, to deposit a continuous layer of the heat sealable coating on said film.

Synthetic organic thermoplastic films which may be coated according to our invention include those produced from polymers of propylene, high density polymers of ethylene, polymers of butene-1 and 4-methyl pentene-1, block copolymers of one or more of these polymers, polyesters such as polyethylene terephthalate, polyamides such as polyhexamethylene adipamide, polyhexamethylene sebacamide or polycaprolactam and oxy-methylene polymers and copolymers. The polymers or copolymers may be mixed with additives e.g. stabilisers, pigments.

Preferably the dispersion contains from 1% to 3% by weight of its polymer solids content of said anti-static agent.

It is preferred to use the alkali or alkaline earth metal salt of said sulphonated condensation product.

Preferred aromatic hydrocarbons are naphthalene and alkyl naphthalenes.

Our invention also comprises the resulting coated films.

It is preferred that the said dispersion contains no other ionic surface-active agent so that the adhesion to the base film is not impaired. However, the presence of very small amounts, up to 0.5%, by weight of its polymer solids content of ionic surface-active agents which may have been used in the manufacture of the polymer dispersion can in some cases be tolerated. For example, it may be desirable to manufacture the heat-sealable polymer dispersion by a dispersion polymerisation process using such small amounts of

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cationic surface-active agents or anionic surface-active agents such as the alkali metal salts of sulphated or sulphonated long chain aliphatic alcohols.

5 If desired, the wetting characteristics of the said dispersion may be improved by the inclusion therein of up to 2% by weight based on the weight of the polymer solids of a non-ionic surface-active agent. 70

10 It is preferred to add any non-ionic surface-active agent used in our process to the polymer dispersion rather than before its manufacture by polymerisation. 75

As examples of suitable non-ionic surface-active agents that may be used we cite the condensation products of ethylene oxide with fatty acids, or with fatty acid amides, ethylene oxide/propylene oxide copolymers, polyoxyethylated nonyl phenol, polyoxyethylated octyl cresol, polyoxyethylated alkyl alcohols such as the oleyl and cetyl alcohols and hydrolysed polyvinyl acetate. Particularly suitable quantities of non-ionic surface-active agent for use in our invention are from 0.4 to 1.5% by weight based on the weight of the polymer solids. 80

When our process is used to coat films of polyolefines such as polypropylene, it is normally necessary first to activate the film surface by any of the known methods for improving the adhesion of coatings thereto, for instance to subject it to corona discharge treatment, or to treatment with ozone or chemical oxidising agents such as halogens, potassium permanganate and chromic acid. Of these treatments the corona discharge treatment is preferred because of its effectiveness and because it is a dry process and is readily carried out. 85

30 40 As the heat-sealable coating polymer there may be used any polymer, including copolymer, which can be heat sealed on the film to which it is applied by standard heat sealing equipment (see H.P. Zade, "Heat Sealing and High Frequency Welding of Plastics" Temple Press, London, 1959). 90

Because they give hard coatings and high heat seal strengths and because of their resistance to moisture and low gas permeability, the heat-sealable coatings which are preferred are the copolymers of vinylidene chloride in major proportion, with another mono-ethylenically unsaturated compound copolymerisable therewith such as methyl acrylate, ethyl acrylate, 95

50 55 methyl methacrylate, methacrylamide, methyl vinyl ether, ethyl vinyl ether, methyl vinyl ketone and acrylonitrile, for instance copolymers containing between 80% and 95% by weight of vinylidene chloride and up to 20% of acrylonitrile. It is particularly preferred to use terpolymers of vinylidene chloride with such copolymerisable monomers and additionally an ethylenically unsaturated mono-carboxylic acid or polycarboxylic acid or a 100

60 65 partial ester of a monoethylenically unsaturated

polycarboxylic acid which is preferably present in an amount of from 0.5 to 5% by weight of the copolymer. Examples of such acids are acrylic and methacrylic acids, maleic acid, fumaric acid, itaconic acid, aconitic acid, citraconic acid and mesaconic acid. The presence of such acidic monomers in these copolymers has a beneficial effect on the adhesion of the copolymer to the base film; in general, the use of higher proportions than 5% has an undesirable effect on the heat stability of the product. 105

Other heat-sealable polymer coatings which may be applied as dispersions are polyvinyl acetate, partially hydrolysed polyvinyl acetate, butadiene/acrylonitrile copolymers, butadiene/styrene copolymers, butadiene/methyl methacrylate copolymers, butadiene/methyl methacrylate/styrene copolymers, methyl methacrylate/methacrylic acid copolymers, copolymers of terephthalic acid and another dicarboxylic acid with a glycol, e.g. those containing no more than 4.0 molecular proportions of combined terephthalic acid to one molecular proportion of combined sebacic acid: copolymers of vinylidene chloride and vinyl chloride, or with methyl or ethyl acrylate, copolymers of vinyl acetate with ethylene or with vinyl propionate and copolymers of vinyl chloride with ethylene, or with vinyl acetate. 110

It will be appreciated that the concentration and particle size of the polymer in the heat-sealable coating dispersion will be chosen so that a continuous heat-sealable layer is formed. Normally a concentration of at least 20% by weight of the dispersion would be used. 115

The coating may be applied by any suitable technique such as by roller-coating, spraying, doctor-knife coating or air-knife coating and the coating may be dried off at any temperature above 50°C. Preferred drying temperatures are from 100 to 140°C. 120

The coating dispersion may contain other additives, for instance, antioxidants, dyes, pigments, lubricants, anti-blocking agents and ultra violet light stabilisers. It is also useful to add slip agents, i.e. comminuted solids which are insoluble in the heat-sealable coating for instance, starch, talc, zinc oxide, calcium carbonate, magnesium carbonate, diatomaceous earths such as "Superfloss", silica, kaolin, titanium dioxide, triferric tetroxide and other inorganic oxides, carbonates, silicates, aluminates and aluminosilicates and finely dispersed polymers such as polypropylene and polyvinyl chloride, the particle size of the slip agent being normally in the range 0.1—20 microns, and preferably for best effect in the range 0.2—5 microns. It is also preferable to include an anti-blocking agent which melts at a temperature above the maximum temperature likely to be encountered during storage of the coated film and which is insoluble in the coating. Examples of suitable 125

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anti-blocking agents include natural waxes, paraffin wax, microcrystalline waxes, beeswax, carnauba wax, montan wax and synthetic waxes such as hydrogenated castor oil, chlorinated hydrocarbon waxes, long chain fatty acid amides.

5 The coated films used in this invention may be unoriented or may be oriented in one or both directions in the plane of the film and if oriented in both directions the orientation may be equal in these directions, or unequal with the higher degree of orientation in a preferred direction (usually the longitudinal direction). The oriented films may be heat set either before or after the coating treatment.

The films of this invention whether oriented by stretching in one or both directions or not may be used for most of the applications for which polythene, cellulose ester or polyethylene terephthalate films have been used in thicknesses between 0.00025 inch and 0.01 inch, for instance as packaging films.

Our invention is illustrated by the following Examples in which all parts are expressed as parts by weight.

The copolymer dispersions used in all the Examples were made by an emulsifier-free aqueous dispersion polymerisation process using an ammonium persulphate/sodium metabisulphite catalyst system.

EXAMPLE 1.

A 0.0005 inch thick, biaxially drawn, heat set film of isotactic polypropylene was sub-

jected to corona discharge treatment so as to reduce its contact angle with water from 90° to 70°. It was then coated with gravure rolls with a dispersion of the following composition:

50 parts of a tercopolymer of vinylidene chloride / acrylonitrile / acrylic acid (91:9:2).
 50 parts of water.
 0.5 part of the sodium salt of a sulphonated condensate of formaldehyde and naphthalene.
 1 part of candelilla wax dispersed with 0.2 part of a polyoxyethylated cetyl alcohol.
 The coated film was dried at 80° C. to produce a clear coating 1×10^{-4} inch thick.

EXAMPLE 2.

The procedure outlined in Example 1 was repeated, the only difference being that 1 part instead of 0.5 part of the sodium salt of a sulphonated condensate of formaldehyde and naphthalene was used.

A control experiment was carried out using the procedure in Example 1 but omitting the anti-static agent.

The properties of the coated films obtained according to the above examples are set out in the Table following.

EXAMPLE 3.

The procedure outlined in Example 1 was repeated but using a latex of:

50 parts of a tercopolymer of vinylidene

Example	Heat Seal Strength ^a (g./in.)	Blocking Value ^b at 38° C. (g.)	Surface Resistivity ^c at 50% R.H. (ohm.cm./cm.)
1	250	45	5×10^{11}
2	240	60	2×10^{10}
Control	220	75	$>2 \times 10^{14}$

^a — The heat seals were made at 130° C./5 p.s.i. for 2 seconds with a 'Sentinel' heat sealer one inch wide by 12 inches long; (Sentinel is a Registered Trade Mark).

^b — Blocking value was determined in the following manner: Two layers of the coated film were superimposed under a load of $\frac{1}{3}$ p.s.i. for 20 hours at 38° C. One layer was attached to one of a pair of rectangular parallel plates 4" \times 3", the other layer being attached to the second plate. The plates were slowly drawn apart in such a way as to allow the layers to peel away from one another symmetrically from two opposite edges of the plates. The maximum force just before separation was measured.

^c — The surface resistivity measurements were recorded after the sample had been stored for 2 minutes to allow it to come into equilibrium with the recorded humidity.

chloride : acrylonitrile : itaconic acid (90: 8: 2).
 1.0 part of the sodium salt of a sulphonated condensate of formaldehyde and naphthalene.
 5 1.0 part of a candelilla wax with 0.2 part of a polyoxyethylated cetyl alcohol.
 The coating was dried at 120° C to produce a clear coating 1×10^{-4} inch thick.

EXAMPLE 4.

The procedure outlined in Example 2 was repeated replacing the sodium salt of a sulphonated condensate of formaldehyde and naphthalene with the sodium salt of a sulphonated condensate of formaldehyde and a methyl naphthalene. The properties of the coated film obtained according to Examples 3 and 4 are set out in the Table below.

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Example	Heat Seal Strength grams/inch	Blocking Value at 38°C grams	Surface Resistivity at 50% R.H. ohm cm/cm
3	190	40	5×10^{11}
5	210	50	5×10^{12}

20 WHAT WE CLAIM IS:—

1. A process which comprises coating the surface of a synthetic organic thermoplastic film with an aqueous dispersion of a heat-sealable polymer, said dispersion containing from 0.5% to 5.0% by weight of its polymer solids content of an ionic antistatic agent comprising the metal, ammonium or amine salt of the sulphonated condensation product of formaldehyde and an aromatic hydrocarbon, and thereafter drying the coated film, to deposit a continuous layer of the heat-sealable coating on said film.
 2. A process according to claim 1 in which said dispersion contains up to 2% by weight based on the weight of the polymer solids of a non-ionic surface-active agent.
 3. A process according to claim 1 or claim 2 in which the synthetic organic thermoplastic film is produced from polypropylene.
 40 4. A process according to claim 1 or claim 2 in which the synthetic organic thermoplastic film is produced from polyethylene terephthalate.
 5. A process according to any one of the preceding claims in which the ionic antistatic agent comprises an alkali or alkaline earth metal salt of said sulphonated condensation product.
 6. A process according to any one of the preceding claims in which the aromatic hydrocarbon comprises naphthalene or an alkyl naphthalene.
 7. A process according to claim 2 in which the non-ionic surface-active agent is added to the polymer dispersion.
 55 8. A process according to any one of the preceding claims in which the film surface is first activated to improve the adhesion of

the coating thereto.

9. A process according to claim 8 in which the film is subjected to corona discharge treatment.

10 10. A process according to claim 8 in which the film is treated with a chemical oxidising agent.

11. A process according to any one of the preceding claims in which the heat-sealable coating comprises a copolymer of vinylidene chloride in a major proportion with another monoethylenically unsaturated compound copolymerisable therewith.

12. A process according to claim 11 in which the heat-sealable coating comprises a tercopolymer of vinylidene chloride with another monoethylenically unsaturated compound and from 0.5% to 5% by weight of the tercopolymer of an ethylenically unsaturated monocarboxylic or polycarboxylic acid or a partial ester of a monoethylenically unsaturated polycarboxylic acid.

13. A process according to any one of the preceding claims in which the heat-sealable coating dispersion contains at least 20% by weight of the heat-sealable polymer.

14. A process according to any one of the preceding claims in which the coating dispersion further contains a slip agent as hereinbefore defined.

15. A process substantially as hereinbefore described with particular reference to Example 1 and part 1 of Example 2 accompanying this specification.

16. A process substantially as hereinbefore described with particular reference to Examples 3 and 4 accompanying this specification.

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17. Coated film whenever made by a process according to any of the preceding claims.

WALTER SCOTT,
Agent for the Applicants.

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